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Formation Mechanism of Needle-like α -FeO Particles Grown Along the c Axis and Characterization of Precursorily Formed β -FeO (Commemoration Issue Dedicated to Professor Toshio TAKADA On the Occasion of His Retirement)

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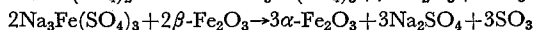
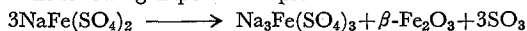
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Formation Mechanism of Needle-like α -Fe₂O₃ Particles Grown Along the c Axis and Characterization of Precursorily Formed β -Fe₂O₃

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The formation mechanism of needle-like α -Fe₂O₃ particles prepared by calcination of a mixture of iron (III) sulphate and sodium chloride was studied through X-ray diffraction, SEM and TEM measurements. These particles are grown along the c axis. The reaction process was found to include the following important steps:



The precursorily formed β -Fe₂O₃ particles could be isolated for characterization by X-ray diffraction, SEM, TEM, magnetic measurement, and Mössbauer spectroscopy. This material is isostructural with bixbyite and the lattice constant is $a_0 = 9.398 \text{ \AA}$. As for the magnetism, it is an antiferromagnet with a Néel temperature of 119 K.

KEY WORDS: Needle-like α -Fe₂O₃/ β -Fe₂O₃ /Cubic iron oxide/ Anti-ferromagnet/ Mössbauer effect/

INTRODUCTION

α -Fe₂O₃ particles with various morphologies have been used widely as a raw material for preparation of γ -Fe₂O₃, a useful magnetic recording material, and other ferrites. The morphological control has been studied by many researchers. Matijević et al., for example, obtained particles with various shapes such as cube, sphere, and spindle by forced hydrolysis of acidified ferric salt solutions at elevated temperatures^(1,2,3). But the orientation of the crystalline axes within those particles has not been reported except for the case of the cubic particles. Tallman and Gulbransen reported the morphology and growth mechanism of α -Fe₂O₃ whiskers, which are blade-like platelets, formed on metallic iron at 400~500°C in dry oxygen^(4,5). They concluded that the platelets consisted of twinned crystals and that the blade axis and the blade face plane were $[\text{II}20]$ and $(\text{I}101)$, respectively. We have reported that needle-like particles with the hexagonal c axis along the longitudinal direction could be obtained by calcination of a mixture of iron (III) sulfate, Fe₂(SO₄)₃, and an alkaline salt such as sodium chloride and sodium sulphate⁽⁶⁾. To our knowledge, this is the only study reporting the formation of needle-like α -Fe₂O₃ particles grown along the c axis. This paper will outline the formation mechanism. We have been keenly interested in the mechanism, because the formation of elongated hexagonal prisms is contradictory to the common sense that

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the closed packed c plane tends to grow.

It is very characteristic that β -Fe₂O₃ has been found to appear intermediately in the reaction process. There are three polymorphs, α -, β -, and γ -forms, of Fe₂O₃ among which α - and γ -Fe₂O₃ have already been well-known. However, there have been very few reports about β -Fe₂O₃. Bonnevie-Svendsen was the first to announce the existence of β -Fe₂O₃, which was prepared by hydrolysis of FeCl₃·6H₂O⁷⁾. Cubic structure with a lattice constant of $a_0=9.40$ Å was assigned. Geller et al.⁸⁾ and Grant et al.⁹⁾ 'predicted' the existence of a cubic polyform from crystallographic considerations on the In₂O₃-Fe₂O₃ and Sc₂O₃-Fe₂O₃ systems. Lina Ben-Dor et al.^{10,11)} reported chemical vapour deposition of β -Fe₂O₃ films consisting of fine particles (~ 500 Å) from iron trifluoroacetylacetone at 300°C onto various substrates. The films were characterized by X-ray diffraction (XRD), SEM and Mössbauer spectroscopy. However, the films were found to be contaminated with a large amount of α -Fe₂O₃. We successfully isolated pure and bulky particles ($\approx 1\mu\text{m}$) of β -Fe₂O₃. In this paper, we report some magnetic properties and the role of this material in the formation process of the α -Fe₂O₃ particles with the unique morphology.

EXPERIMENTAL

The starting materials were Fe₂(SO₄)₃ and NaCl of the reagent grade. These were thoroughly mixed in an agate mortar with various ratios. The mixtures were placed on Al₂O₃ trays and calcined in the air under various conditions with respect to temperature and time. After cooling to room temperature, the reaction products were dispersed in distilled water, filtered, and washed with distilled water. Phase identification and determination of lattice parameters were carried out by means of powder X-ray diffraction using graphite-monochromated CuK α radiation. The diffractometer was Rigaku RU-200. Si (99.999%) powder was used as an internal standard when necessary. The measurement was extended to 1073 K using a platinum furnace. Magnetic properties of β -Fe₂O₃ were measured with a SQUID magnetometer (SHE) between 4.2 K and 300 K. The Mössbauer effect (ME) was measured in the same temperature range using a ⁵⁷Co/Rh source. Metallic iron was used as a control sample for velocity calibration and as the isomer shift reference. Identification of crystalline phases, observation of the particle shape and size were carried out by means of TEM (JEOL-7A) and SEM (JEOL-200T). TG-DTA measurements were made between 300 K and 1073 K in the air using an apparatus of Rigaku TG4-DT6.

RESULTS AND DISCUSSION

I. Formation Mechanism of Needle-like α -Fe₂O₃ Particles —Part 1

When a mixture of Fe₂(SO₄)₃ and NaCl was heated in the air above 700°C, the final product was always a mixture of α -Fe₂O₃ and Na₂SO₄. However, as reported in our previous paper⁶⁾, the morphology of the α -Fe₂O₃ particles depended on the composition of the starting mixture, heating temperature, and time; the composition, especially, had a crucial effect. Needle-like particles with a length

of $1\sim 15\ \mu\text{m}$ and a width of $\sim 1\ \mu\text{m}$ could be obtained uniformly by calcination of the mixture with a molar ratio of $\text{Fe}_2(\text{SO}_4)_3 : \text{NaCl} = 1:2$ at 700°C for 1 hr. Typical SEM and TEM micrographs of these particles are given in Fig. 1 (A) and (B). Both the top and lateral planes of the hexagonal prisms are smooth, without steps or cracks, at the magnification used by us. Electron diffraction patterns and the corresponding dark field images showed the longitudinal direction to be $[0001]$.

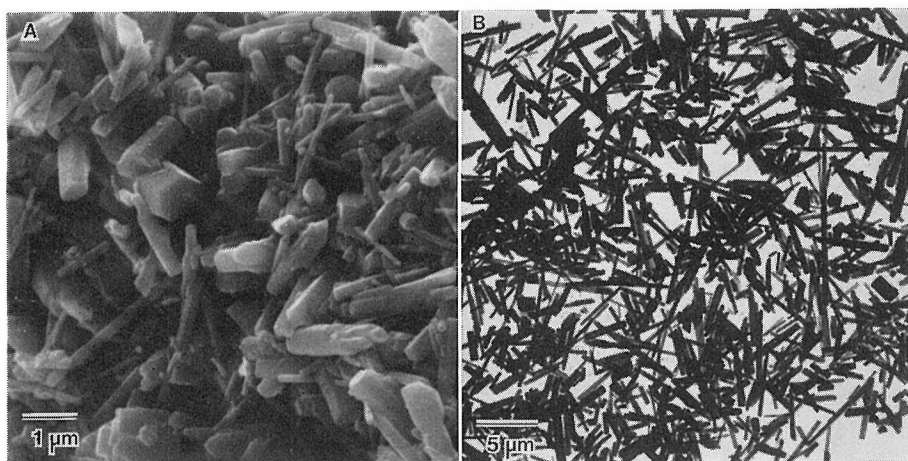


Fig. 1. SEM (A) and TEM (B) micrographs of needle-like α -Fe₂O₃ particles.

The reaction process was studied by calcining the starting mixtures at lower temperatures for 1 h to slow down the reaction rate. Summarized in Table 1 are the intermediate compounds identified by XRD obtained from the 1:2 starting mixture. These results suggested that the reaction process consisted of the following three important stages.

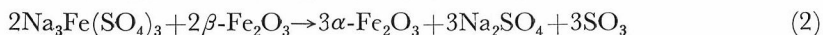
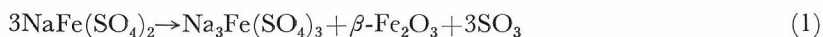
Table I. Compounds identified by XRD contained in the products obtained by calcination of the mixture with a molar ratio of $\text{Fe}_2(\text{SO}_4)_3 : \text{NaCl} = 1:2$ at various temperatures for 1 hr in the air.

Compound	Calcination Temperature ($^\circ\text{C}$)									
	200	300	400	500	575	600	625	650	675	700
NaCl	○	○	○							
$\text{Fe}_2(\text{SO}_4)_3$	○	○	○	○						
$\text{NaFe}(\text{SO}_4)_2$	○	○	○	○	○	○				
$\text{Na}_3\text{Fe}(\text{SO}_4)_3$			○	○	○	○	○			
Na_2SO_4								○	○	○
β -Fe ₂ O ₃				○	○	○	○	○		
α -Fe ₂ O ₃						○	○	○	○	○

- 1) At the first stage, $\text{NaFe}(\text{SO}_4)_2$ was produced by reaction of $\text{Fe}_2(\text{SO}_4)_3$ and NaCl.
- 2) At the second stage, $\text{NaFe}(\text{SO}_4)_2$ was decomposed gradually to β -Fe₂O₃ and $\text{Na}_3\text{Fe}(\text{SO}_4)_3$.

- 3) At the last stage, α -Fe₂O₃ and Na₂SO₄ were produced by reaction of Na₃Fe(SO₄)₃ and β -Fe₂O₃.

Though the reaction at the first stage remains somewhat unresolved, the second and the third stages may be expressed by the following equations.



The precursory formation of β -Fe₂O₃ has been found to be essentially important for the formation of needle-like α -Fe₂O₃ particles as will be described later.

II Formation Process and Characterization of β -Fe₂O₃

A SEM photograph of the product obtained by calcination of the 1:2 mixture at 550°C for 1 hr is shown in Fig. 2. Cubic particles like the one indicated by an arrow correspond to β -Fe₂O₃. According to XRD, the product contained two

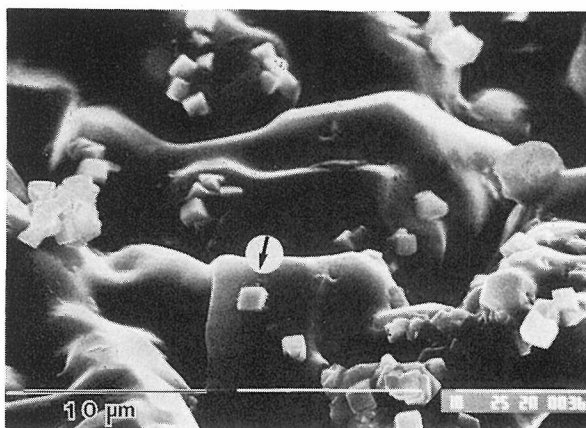


Fig. 2. A SEM micrograph of the product obtained by calcination of the 1:2 mixture at 550°C for 1 hr. An arrow point to a β -Fe₂O₃ particle.

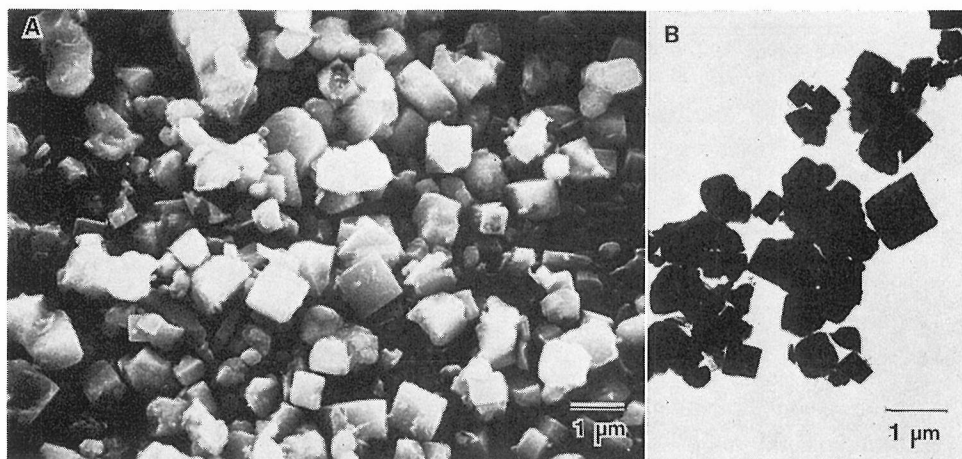


Fig. 3. SEM (A) and TEM (B) micrographs of isolated β -Fe₂O₃ particles.

other phases which were $\text{NaFe}(\text{SO}_4)_2$ and $\text{Na}_3\text{Fe}(\text{SO}_4)_3$. However, the two latter phases could be identified in the photograph only as a homogenous bulk with a wavy smooth surface like that of a quenched liquid. Figure 3 shows SEM (A) and TEM (B) micrographs of the β - Fe_2O_3 particles isolated by washing with distilled water.

The XRD pattern obtained is shown in Fig. 4. All the diffraction peaks were

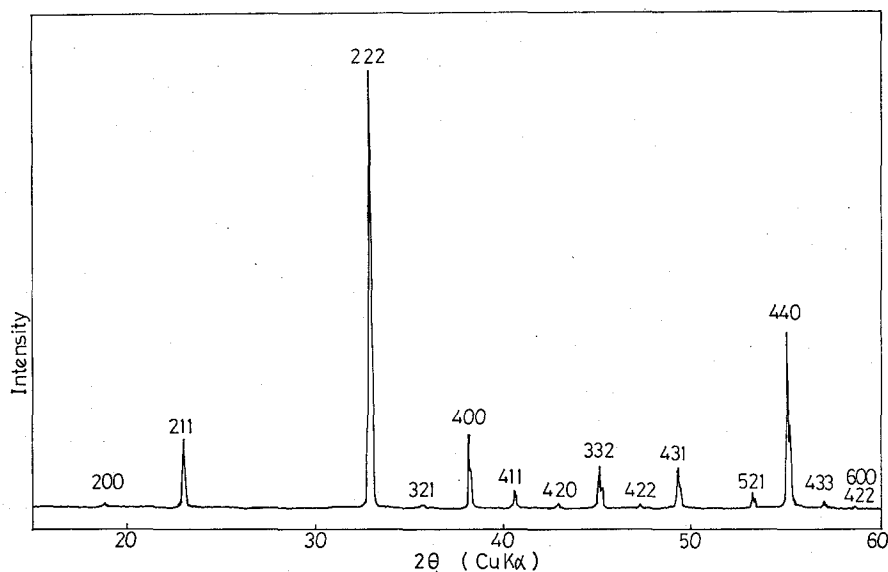


Fig. 4. XRD pattern of β - Fe_2O_3 .

very sharp and could be assigned to the bixbyite-type structure with space group $\text{Ia}\bar{3}$ ⁷⁾. The cell dimension was determined to be $a_0 = 9.398 \pm 0.001 \text{ \AA}$. The XRD data are summarized in Table 2. It should be emphasized here that any diffraction peak assignable to α - Fe_2O_3 could not be detected at all even by a very careful measurement. Electron diffraction measurements confirmed that each particle was a single crystal. It should be noted in Fig. 3 that β - Fe_2O_3 tends to form cubic particles with the $\{100\}$ facets. However, the shape is not perfect, some corners being apparently torn off. We have supposed that this results from the following growth mechanism. β - Fe_2O_3 nucleates on thermal decomposition of $\text{NaFe}(\text{SO}_4)_2$, when $\text{Na}_3\text{Fe}(\text{SO}_4)_3$, which is simultaneously formed, and residual $\text{NaFe}(\text{SO}_4)_2$ produce a eutectic liquid phase around the nuclei. The eutectic nature was suggested not only from Fig. 2 but also from the fact that pure $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ remains solid at 550°C as found by our independent experiment. Elements necessary for the growth of the nuclei are supplied from $\text{NaFe}(\text{SO}_4)_2$ through the liquid.

DTA and XRD measurements at elevated temperatures showed that β - Fe_2O_3 began to be transformed to α - Fe_2O_3 at about 600°C . The transformation was gradual but was accelerated at higher temperatures. It finished within a few minutes at 780°C . The α - Fe_2O_3 particles were also single-crystalline cubic particles. Topotactic relations between these polymorphs are under examination.

Table II. List of the X-ray data of β -Fe₂O₃ crystallizing in the cubic bixbyite structure; $a_0=9.398$ Å.

d (obs.)	d (cal.)	(I/I ₀)	(H K L)
4.70	4.70	<1	(200)
3.838	3.837	15	(211)
2.714	2.713	100	(222)
2.513	2.512	1	(321)
2.350	2.350	16	(400)
2.216	2.215	5	(411)
2.102	2.101	1	(420)
2.005	2.004	10	(332)
1.919	1.918	1	(422)
1.844	1.843	9	(431)
1.717	1.716	4	(521)
1.662	1.661	40	(440)
1.612	1.612	2	(433)
1.567	1.566	<1	(600), (442)
1.525	1.525	5	(611), (532)
1.487	1.486	1	(620)
1.451	1.450	4	(541)
1.417	1.417	19	(622)
1.387	1.386	5	(631)
1.357	1.356	3	(444)
1.330	1.329	1	(543)
1.304	1.303	1	(640)
1.280	1.279	3	(721), (633), (552)
1.257	1.256	1	(642)
1.194	1.194	1	(732), (651)
1.176	1.175	3	(800)
1.158	1.157	2	(811), (741), (554)
1.141	1.140	1	(820), (644)
1.124	1.123	1	(653)
1.108	1.108	1	(822), (660)
1.093	1.093	2	(831), (743)
1.079	1.078	4	(662)
1.051	1.051	2	(840)
1.038	1.038	<1	(833)
1.026	1.025	<1	(842)
1.014	1.013	1	(921), (761), (655)
1.002	1.002	<1	(664)
.991	.991	1	(851), (754)
.970	.969	1	(932), (763)
.959	.959	3	(844)
.950	.949	1	(941), (853)
.940	.940	1	(860)
.931	.931	<1	(772)
.922	.922	2	(862)
.913	.913	<1	(943)
.905	.904	2	(666)
.896	.896	2	(952), (765)

Temperature dependences of the magnetic susceptibility, χ , and the inverse susceptibility, χ^{-1} , are shown in Fig. 5. Field dependence of the magnetization at 4.2 K is also shown in Fig. 6. These data clearly indicate that β - Fe_2O_3 is an

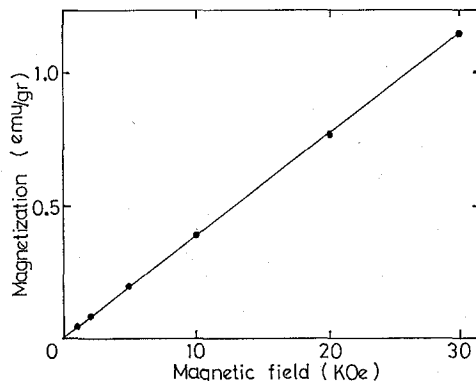


Fig. 6. Magnetic field dependence of the magnetization of β - Fe_2O_3 at 4.2 K.

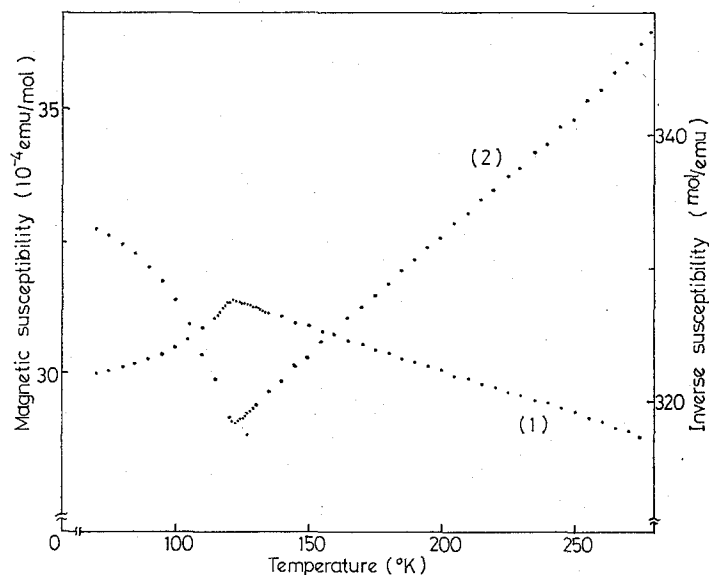


Fig. 5. Temperature dependence of the magnetic susceptibility (1) and its inverse (2) of β - Fe_2O_3 at 5 kOe.

antiferromagnetic substance with a Néel temperature of 119 K. The asymptotic Néel temperature and the effective Bohr magneton number were derived from the Curie-Weiss law holding in the paramagnetic state. The former was -1635 K and suggested a very strong antiferromagnetic exchange interaction between the Fe^{3+} ions. The latter was 6.64, which was slightly larger than the expected spin-only value of 5.92 for a Fe^{3+} ion in high spin state. However, similar values of 6.4 and -2940 K were reported also for α - Fe_2O_3 ⁽¹²⁾. As the cation sites in the bixbyite structure form an approximately face-centered-cubic lattice which does not

allow a simple collinear antiferromagnetic spin structure, a neutron diffraction study is of great interest and is in progress. Figure 7 shows the ME spectra at 300 K and 4.2 K. The spectrum at 300 K looks like a single quadrupole doublet with an isomer shift of 0.38 mm/s and a quadrupole splitting of 0.75 mm/s, though there

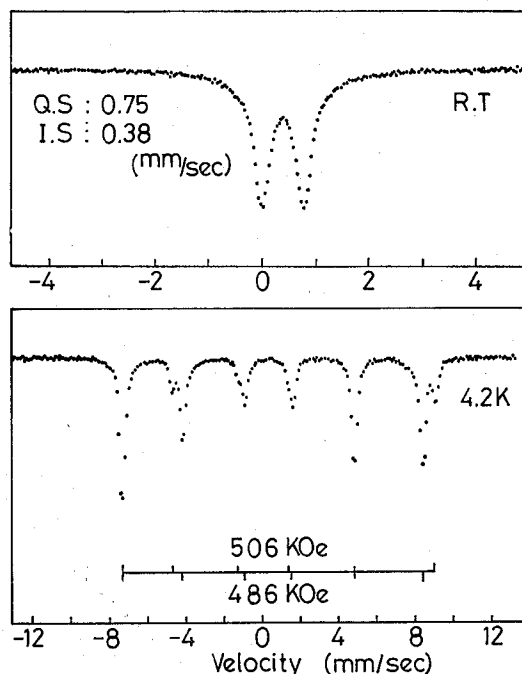


Fig. 7. ME spectra of β -Fe₂O₃ at 300 K and 4.2 K.

are two kinds of cation sites, 24 d and 8 b, with a relative abundance of 3:1. However at 4.2 K, two sets of magnetic hyperfine patterns with hyperfine fields of 506 kOe and 486 kOe can be seen, and the relative intensity is near 3:1. Measurements at intermediate temperatures confirmed the antiferromagnetic transition at 119 K. The spectra at low temperatures are useful in elucidating the spin structure. Further details will be reported elsewhere together with the results of the neutron diffraction measurements.

III Formation Mechanism of Needle-like α -Fe₂O₃ Particles—Part 2

In this section we shall show the key role of β -Fe₂O₃ in the formation process of the needle-like α -Fe₂O₃ particles, and a probable formation mechanism will be discussed in brief. It is interesting to study the reaction of well-characterized β -Fe₂O₃ and Na₃Fe(SO₄)₃ particles. Single phase β -Fe₂O₃ particles, isolated as described in the preceding section, and Na₃Fe(SO₄)₃, prepared by condensation of an aqueous solution containing Na₂SO₄ and Fe₂(SO₄)₃ in a molar ratio of 3:1, were thoroughly mixed in a molar ratio of 1:1 as given in eq. (2) and heated on an alumina tray at 700°C for 1 h in the air. The product was a mixture of α -Fe₂O₃ and Na₂SO₄ as found by XRD. A SEM observation of the α -Fe₂O₃ particles isolated

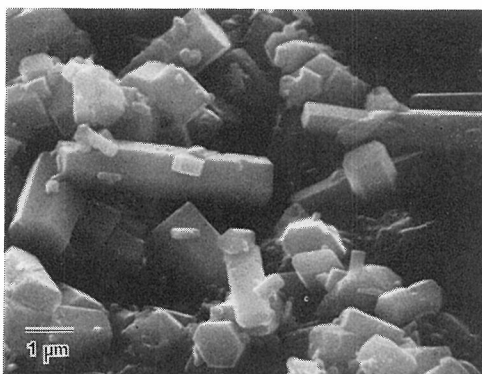


Fig. 8. A SEM micrograph of α -Fe₂O₃ obtained by calcination of the mixture with a molar ratio of β -Fe₂O₃: Na₃Fe(SO₄)₃=1:1 at 700°C for 1 hr in the air.

by washing with distilled water is shown in Fig. 8. It could be clearly seen that thick hexagonal prisms of α -Fe₂O₃ were formed from the mixture, though a similar heat treatment of each constituent alone never produced such particles. It is interesting to point out here that the area of a hexagonal top plane is, generally, similar to that of the (100) or (110) plane of an original β -Fe₂O₃ particle.

From various experimental results including those mentioned above, we can at least mention the following important steps in the formation of beautiful hexagonal-prismatic α -Fe₂O₃ particles. β -Fe₂O₃ seems to be dissolved into and precipitated as α -Fe₂O₃ from molten Na₃Fe(SO₄)₃ (m.p. \approx 600°C). The dissolution does not extend deep into a particle of β -Fe₂O₃ before α -Fe₂O₃ precipitates on it epitaxially. The inner part can be automatically transformed into α -Fe₂O₃ which is stabler at 700°C. Elements necessary for the particle growth are supplied from Na₃Fe(SO₄)₃. The decomposition of this sulfate seems to be promoted by the presence of either α - or β -Fe₂O₃: the liquid sulfate can remain stable when alone as found by an independent experiment. The participation of molten Na₃Fe(SO₄)₃ gives rise to the well-defined crystal habit.

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